TRANSESTERIFICATION OF GLYCEROL WITH DIMETHYL CARBONATE TO GLYCEROL CARBONATE OVER ASH-, CLAY- BASED AND STRONTIUM-ALUMINUM MIXED OXIDE CATALYSTS

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By

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LIST OF SYMBOLS

Symbol	Description	Unit
$^{\circ}A$	Angstrom	-
C	Conversion	-
Y	Yield	-
H	Hysteresis type	
N_G	Concentration of glycerol	mol
N_{Gh0}	Initial concentration of glycerol	
N_{GC}	Concentration of glycerol carbonate	mol

LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
CFA	Coal Fly Ash
DMC	Dimethyl Carbonate
DEC	Diethyl Carbonate
EDX	Energy Dispersive X-ray
EPA	Environmental Protection Agency
FAME	Fatty Acid Methyl Ester
FTIR	Fourier Transform Infrared
FFAs	Free Fatty Acids
H_	Hammett Function
HT	Hydrotalcites
IUPAC	International Union of Pure and Applied Chemistry
OPA	Oil Palm Ash
Rpm	Revolutions Per Minute
SEM	Scanning Electron Micreoscopy
TGA	Thermogravimetric Analyzer
XRD	X-ray Diffraction

TRANSESTERIFIKASI GLISEROL DENGAN DIMETIL KARBONAT KEPADA GLISEROL KARBONAT MENERUSI PEMANGKIN-PEMANGKIN BERASASKAN ABU, TANAH LIAT DAN CAMPURAN OKSIDA STRONTIUM-ALUMINUM

ABSTRAK

Pertumbuhan global dalam pengeluaran biodiesel sepanjang dekad yang lalu telah membawa kepada adanya kuantiti besar gliserol sebagai produk sampingan proses transesterifikasi trigliserida. Gliserol (GL) adalah bahan mentah serba guna yang boleh digunakan untuk menghasilkan bahan kimia seperti gliserol karbonat (GC) yang boleh dihasilkan melaluih transesterifikasi gliserol dengan karbonat dimetil (DMC) ke atas pemangkin asas. Dalam kerja ini , dolomit , tanah liat kaya natrium, abu kelapa sawit dan K- zeolite disintesis abu terbang telah digunakan sebagai kos rendah pemangkin asas heterogen untuk sintesis GC dari GL dan DMC. Kajian ini telah dijalankan dalam reaktor kelompok pada keadaan tindak balas yang berbeza, (1-7 % berat) muatan mangkin ; (1:01-4:01) DMC : Nisbah molar GL ; (55-75 ^{O}C) suhu tindak balas dan (0.5-2 h) masa tindak balas. Pada keadaan yang terbaik operasi 5 % berat muatan pemangkin; 3:1 nisbah molar DMC:GL; 75 ^{O}C suhu tindak balas dan 1.5 jam masa tindak balas, hasil GC masing-masing adalah 98.4 %, 97.34 %, 96.4% dan 94 % untuk Na- tanah liat, abu kelapa sawit, K- zeolite dan dolomit. Dari segi kebolehgunaan pemangkin dan larut lesap, semua pemangkin mengalami kelemahan larut lesap spesies logam dalam julat antara (4,23-31 %) dan prestasi pemangkin terbaik telah diperolehi oleh Na- tanah liat di mana larut lesap minimum telah berlaku (4.23%) berbanding dengan kos rendah pemangkin yang lain dan ia telah digunakan dengan jayanya selama empatkitaran. Strontium- aluminium

pemangkin campuran oksida juga telah dibangunkan untuk menjadi pemangkin heterogen lebih stabil dan tidak larutlesap untuk sintesis GC dari GL dan DMC. Pemangkin itu dihasilkan oleh kaedah presipitasi bersama dan dikalsinasi pada suhu 900 ^{O}C untuk 12 jam . Nisbah atom optimum dioptimumkan di Sr / Al = 0.5.Hasil GC adalah 99.6% pada keadaan tindak balas : 3 % berat muatanpemangkin, 2:1 DMC : Nisbah molar GL ; 70 ^{O}C suhu tindak balas : 1 jam masa tindakbalas. Larut lesap spesies logam adalah serendah 0.19% selepas kitaran yang kelima yang boleh dikaitkan dengan pembentukan fasa $Sr_3Al_2O_6$ perovskit yang menstabilkan ion Sr dari larut lesap. Secara keseluruhan, pemangkin kos rendah mempamerkan applikasi yang baik sebagai pemangkin heterogen dengan hasil GC yang tinggi. Dolomite, K-zeolite dan Na- tanah liat telah berjaya digunakan semula untuk empat kitaran yang setanding dengan apa yang dilaporkan dalam literasi dengan kelebihan tambahan bahawa pemangkin tersebut diperbuat daripada sisa dan bahan-bahan semula jadi yang banyak. Campuran oksida Sr-Al pada umumnya ialah pemangkin yang terbaik dari segi hasil dan prestasi di kalangan semua pemangkin yang telah diuji.

TRANSESTERIFICATION OF GLYCEROL WITH DIMETHYL CARBONATE TO GLYCEROL CARBONATE OVER ASH-, CLAY- BASED AND STRONTIUM-ALUMINUM MIXED OXIDE CATALYSTS

ABSTRACT

The global growth in biodiesel production over the past decade has led to the availability of significant quantities of glycerol as a by-product of the triglyceride transesterification process. Glycerol (GL) is a versatile feedstock for producing chemicals such as glycerol carbonate (GC) which can be produced by the transesterification of glycerol with dimethyl carbonate (DMC) over base catalyst. In this work, dolomite, sodium rich clay, oil palm ash and K-zeolite synthesized form fly ash have been utilized as low-cost heterogeneous basic catalysts for GC synthesis from GL and DMC. The study was conducted in a batch reactor at different reaction conditions (1-7 wt%) catalyst loading; (1:1-4:1) DMC:GL molar ratio; (55-75 ^{O}C) reaction temperature and (0.5-2 h) reaction time. At the best operating conditions of 5 wt% catalyst loading; 3:1 DMC: GL molar ratio; 75 ^{O}C reaction temperature and 1.5 h reaction time, the yields of GC obtained were 98.4%, 97.3%, 96.4% and 94% for Na-clay, oil palm ash, K-zeolite and dolomite, respectively. In terms of catalyst reusability and leaching, all catalysts suffered from leaching of metallic species in range between (4.23-31%) and the best catalytic performance was obtained by Na-clay where the minimum leaching was occurred (4.23%) compared to other low-cost catalysts and it was used successfully for four cycle runs. Strontium-aluminum mixed oxide catalyst was also developed in order to have more stable and unleachable heterogeneous catalyst for GC synthesis from GL and DMC. The

catalyst was synthesized by co-precipitation method and calcined at 900 ^{O}C for 12h. The optimum atomic ratio was optimized at Sr/Al=0.5. The yield of GC was 99.6% at reaction conditions of : 3 wt% catalyst loading; 2:1 DMC: GL molar ratio; 70 ^{O}C reaction temperature; 1 h reaction time. The leaching of metallic species was as low as 0.19% after the fifth cycle run which could be attributed to the formation of $Sr_3Al_2O_6$ perovskite phase which stabilize the Sr ions from leaching. Overall, low-cost catalysts exhibited good applicability as heterogeneous catalyst with high GC yield. Dolomite, K-zeolite and Na-clay was successfully reusable for four cycles which comparable with what reported in literature with additional advantage that these catalysts made from waste and naturally abundant materials. Mixed oxide of Sr-Al oxide was generally the best catalyst in term of yield and performance among all catalysts tested.

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CHAPTER ONE

INTRODUCTION

1.0 Introduction

In the last decade, the massive consumption of the crude oil drives the prices to increase dramatically. Nations started to look for energy alternatives to sustain their supply for energy and reduce their dependence on conventional crude oil. Also, the concerns regarding the depletion of conventional oil reserves as well as emissions problem associated with its consumption drive the world to look for renewable and eco-friendly alternatives. One of the promising alternatives is biodiesel. The unique feature about biodiesel that it can be used in the present day diesel engine with no major modification which makes it a good replacement for petro-diesel. Also, the combustion of biodiesel is much less pollutant than petro-diesel (Demirbas, 2009). Biodiesel is a mixture of Fatty Acid Methyl Esters (FAME). Typically, it is produced by transesterfication of triglyceride (vegetable oil) with alcohol, usually methanol or ethanol (Islam et al., 2012). In the last few years, the production of biodiesel increased dramatically around the world. In 2008, the global production of biodiesel was 11 million tons. The growth rate is increasing rapidly due to the commitment of European Union, US and some Asian countries to decrease the dependence on the foreign energy resources as well as greenhouse emissions reduction regulation requirements (Quispe et al., 2013). However, the major challenge in biodiesel industry is the utilization of co-product glycerol. In the transesterfication reaction of Triglyceride, glycerol is produced as 10 % (wt/wt) of FAME (Johnson & Taconi, 2007).

The increase in biodiesel production creates a surplus in glycerol supply market which decreased the prices drastically. For instance, the prices in the US for refined glycerol in 2008 were $1.00 – $3.00/kg where it was in the range of $0.10-$0.50/kg for crude glycerol. By 2016, if the biodiesel production reach 1.4 million m^3 as predicted there will be 150 thousand m^3 of glycerol in the market which is going to push the prices downward and it is going to affect the biodiesel industry undesirably (Quispe et al., 2013).

Glycerol has many applications in food, pharmaceuticals and personal care industries. However, continuous excess volume of glycerol supply cannot be absorbed by the current market. Also, the refined grade of glycerol (99% purity) required by these industries reduce the profitability of the biodiesel production because the glycerol produced by biodiesel plants contains impurities (88% purity) which require more purification. At low prices of glycerol, the purification of crude glycerol produced by biodiesel plants is not feasible (Pathak et al., 2010). According to Haas et al. (2006) study on the cost of biodiesel production, there is a linear relation on the production cost of biodiesel and glycerol prices.

Due to the low prices of glycerol which appeared will not recover since there is a continuous increase in biodiesel production. Also, the improper disposal of glycerol where it is an environmental issue catalyzes the idea of novel use for glycerol (Posada et al., 2012). Extensive research efforts have been done to convert glycerol to valuable products. Under the steady cheap prices of glycerol, the use of glycerol as a feedstock is very attractive.

One of the attractive derivatives of glycerol that gain much interest recently is glycerol carbonate. Glycerol carbonate considered relatively as new material in

industry. It has low flammability, toxicity and vapor pressure. Also, it has a good biodegradability which makes it a potential material in different industrial sectors. It can be used as adhesive, surfactant, solvent in paint industry, cosmetics, detergents, gas separation membrane and polymer synthesis (Ochoa-Gómez et al., 2012). It is produced from glycerol by different methods, such as reaction of glycerol with urea (Wang et al., 2011), carbonation of glycerol with carbon dioxide (Hammond et al., 2011), direct carbonation of glycerol with phosgene (Ochoa-Gómez et al., 2012) and transesterfication of glycerol with alkyl carbonate like diethyl carbonate or dimethyl carbonate (Ochoa-Gómez et al., 2009). The later process starts with non-toxic materials under mild operation conditions and obtains a good glycerol carbonate yield which make it the most attractive process for glycerol carbonate synthesis among other processes (Aresta et al., 2009).

1.1 Problem statement

In recent years, research efforts are ongoing to use glycerol as a platform for chemical synthesis. This route has been driven by a surplus glycerol available on the market with low price. The majority of glycerol produced as by product of biodiesel industry which is suffering from costly handling of glycerol. As glycerol produced by 10 wt% in biodiesel production, biodiesel industry facing a challenge in utilizing huge quantities of glycerol produced as the world is shifting toward biodiesel in sake for renewable environmentally clean energy.

The production of glycerol carbonate from glycerol and alkyl carbonate is promising route to utilize glycerol which in turn affect the biodiesel industry positively. The presence of catalytic material is required for the reaction to proceeds. Homogenous base catalysts offer an excellent conversion of glycerol and glycerol

carbonate yield. However, the use of homogenous base catalysts has some issues affecting the feasibility of the process. First, a separation step required to separate the catalyst from the product is energy incentive which affect the profitability of the process. Furthermore, it requires a neutralization step where acids should be added to neutralize the catalyst which translated as additional cost to the process.

In contrast, heterogeneous catalysts offer some advantages over homogenous one. For example, using heterogeneous catalysts will eliminate the neutralization step required for homogenous catalysts which reduce the waste formation and eliminate the separation cost. Moreover, heterogeneous catalysts can be reusable compared to the homogenous one which opens the doors to design of an efficient continuous process. However, the main challenge in using heterogeneous catalysts in the transesterfication of glycerol is the stability of the catalysts. Still there is ongoing research on the development of heterogeneous catalysts that can be used for many reaction cycles. However, until now all the research that has been conducted observed the deactivation of the heterogeneous catalysts and a dramatic decrease in glycerol carbonate yield on recycling experiments.

Still there is a great chance in finding stable heterogeneous catalyst that can be used commercially in the future. First, waste and natural materials need to be explored in sake to find green and cost effective catalyst. There are some of waste materials and natural clays minerals that have suitable basicity for the transesterification of glycerol with dimethyl carbonate. Oil palm ash, waste generated from palm oil industry, has a high content of potassium that can be used to activate the reaction between glycerol and DMC. Also, coal fly ash, a major waste generated from coal power plant; used to be a good source of aluminum silicate that could be used to synthesize basic zeolite. For clay minerals, dolomite, a mixture of

calcium and magnesium carbonate, and sodium rich clay are promising candidate also due to the availability of alkaline metals in their composition. Synthesized mixed oxides also are another opportunity need to be discovered to find stable and active heterogeneous catalyst for the reaction. Mixed oxide catalysts have been utilized successfully in many catalytic reactions and it shows great activity and stability. As a result, the development of stable, cost effective heterogeneous catalysts for the process is the main motivation for this research.

1.2 Research objectives

The purpose of this research to utilize agricultural waste, clay minerals and mixed oxides searching for cost effective heterogonous catalyst for the transesterification of glycerol and dimethyl carbonate for glycerol carbonate synthesis. The objectives were focused to:

i) Study the feasibility of waste materials (oil palm ash, fly ash), natural clay minerals (dolomite, sodium rich clay) and strontium aluminum mixed-oxide as heterogeneous catalyst for the transesterfication of glycerol and dimethyl carbonate for glycerol carbonate synthesis.

ii) Characterize the developed catalysts to gain more insight on their structure, morphology, composition and porosity.

iii) Investigate the effect reaction parameters such as reaction temperature, amount of catalyst, reaction time and dimethyl carbonate to glycerol molar ratio in the transesterification reaction.

iv) Study the stability and the reusability of the catalysts during the reaction course.

1.3 Scope of the study

The scope of the present study covered the development, characterization and the test of activity of the heterogeneous catalysts derived from waste and natural materials and developed mixed oxide catalyst in transesterification of glycerol with dimethyl carbonate for synthesis of glycerol carbonate. Dolomite, sodium rich clay, oil palm ash were considered on this study for its basic nature that suitable for the reaction herein. Coal fly ash was utilized as a source of aluminum-silicate to synthesize K-zeolite. The K-zeolite was synthesized by the activation of fly ash with potassium hydroxide. All catalysts in the study are characterized using surface area analyzer, Fourier Transform Infrared Spectrometry (FTIR), scanning electron microscopy (SEM), X-ray diffractometer (XRD) and energy dispersive X-ray (EDX).

The transesterfication reaction was conducted in glass batch reactor for the study of the catalytic activity of the developed and utilized catalysts. Important process variables were studied including catalyst loading (wt% of glycerol), dimethyl carbonate:glycerol molar ratio, reaction temperature and reaction time. The reusability of catalysts was tested using appropriate techniques.

Strontium and aluminum metals have been combined on this study for the development of mixed oxide catalyst. The catalyst was developed by co-precipitating of metallic salts of strontium and aluminum in alkali medium. The treatment employed on the mixed oxide catalyst includes determination of optimum calcination temperature to synergize the combined metallic oxides, ratio of metal combination and calcination time to give the best product yield. Same procedure in characterization and testing of catalytic activity that have been performed on the low-cost catalysts was also implemented for the strontium-aluminum mixed oxide.

1.4 Thesis outline

There are five chapters in this thesis. The first chapter has provided a quick overview and motivation on this project.

Chapter two presents a review of the literature. It is divided into eight major sections. The first section gives a review on current biodiesel industry and biodiesel by product glycerol present situation. This is followed by a brief discussion on the properties and potential application of glycerol. After that, the properties and the applications of glycerol carbonate are provided in section three. Then, glycerol carbonate synthesis methods from glycerol are explained in section four. A detailed review on heterogeneous catalysts for the transesterification of glycerol with dialkyl carbonate is presented on section five. Section six, deals with reactions parameters involves on the transesterification of glycerol with DMC. After that, stability and reusability aspects of heterogeneous catalysts in the transesterification reaction of glycerol with DMC are discussed on section seven. Lastly, a short summary based on the literature review is presented on section eight.

Chapter three covers the methodology for the experimental work done in this research. This chapter is distributed to six sections. The first section explains the research activity followed during the study. The second section shows materials and reagents used throughout the project. The bases of catalyst selection and preparation methods of the tested catalyst are discussed on section three. After that, catalyst characterization techniques are given on section four. A general description on experimental reaction setup, reaction analysis and procedures are discussed on section five. Finally, section six deals with the procedures that been followed to test the reusability and leaching of metallic species from the tested catalysts.

Chapter Four presents all the acquired results and discusses on the findings. It is grouped into four main sections. Section one discuss the results of characterization data obtained for low cost catalysts (dolomite, K-zeolite from fly ash, OPA and Na-clay). Section two; compare the catalytic activity of the low-cost catalysts and their stability as well. Characterization of synthesized Sr-Al mixed oxide catalyst is explained on section three while it activity and stability are presented on the last section, section four.

Finally, Chapter Five gives the conclusion and some recommendations for future research. The conclusions are written according to the finding found in Chapter Four. Based on the conclusion, recommendations for future work are suggested.

CHAPTER TWO
LITERATURE REVIEW

2.0 Introduction

This chapter provides a literature review for this study. Section one provides an overview about biodiesel industry and glycerol gluts on the market. Glycerol properties and its current and potential applications are discussed on section two. The chemical and physical properties of glycerol carbonate as well as its applications are presented on section three. Section four reviews the methods that have been used to synthesize glycerol carbonate from glycerol. In detailed discussion on heterogeneous catalyst that been used for glycerol carbonate synthesis from dialkyl carbonate are shown on section five. Section six depicts in-depth discussion on the process parameters involved in transesterification (catalyst loading, dialkyl carbonate to glycerol molar ratio, reaction time and temperature). Finally, section seven focuses on the importance of catalyst reusability and regeneration for the transesterfication process.

2.1 Production of biodiesel and glycerine gluts

Fossil fuels are the major sources of energy, accounting for about 80% of the global energy demand (Sarma et al., 2012). However, they are associated with many problems: they are non-renewable and the reserves are depleting; they have adverse climatic, environmental and health effects; and their prices are erratic due to political crisis in major producing countries. Due to these problems associated with the use of fossil fuels, there is an increasing demand for biofuels as suitable alternatives (Gui et al., 2008; Sarma et al., 2012). The biofuels, apart from being alternatives to fossil-derived fuels, are secure, renewable, non-toxic, have favorable energy balance, have

lower harmful emissions and, therefore, environmentally friendly (Salvi & Panwar, 2012). Recently, there has been a significant increase in their production and use. However, increased biodiesel production leads to glycerol glut, which questions the economic viability of biodiesel industry.

2.1.1 Biodiesel production

The idea to use a renewable resource as a fuel in a diesel engine has been around for over a century. The first recorded use of biodiesel was on August 10th, 1893 by Rudolf Diesel, the inventor of the diesel engine. He was able to use peanut oil to successfully run and provide power from a diesel engine. During his lifetime, he predicted that bio-based fuels would someday become as important as petroleum and coal products (Yusuf et al., 2011).

After Diesel, the low cost and high efficiency of petroleum-based products prevented the advancement of alternative fuels for many years. It was not until the gas scare of the 1970s, that supply and security concerns again prompted interest in developing alternative forms of energy. Solar, wind, geothermal, biomass, and other renewable energies were becoming more and more desirable (Chang et al., 2013). Still, even now, many countries are heavily dependent on fossil fuels to meet their energy needs. The technologies to successfully use many forms of renewable energy sources are not developed enough to use cheaply and efficiently on a widespread scale. Until technology and research progresses far enough, it is important that any new technology has the ability to be implemented into the current infrastructure with little or no difficulties (Armas et al., 2013).

In terms of the energy required in the transportation sector, biofuel is able to meet many of these requirements. It is a renewable resource that can be produced in

many different countries, which helps limit political and security concerns. Also, biofuels can be implemented directly into the current infrastructure and used in modern engines with little or no modifications (Lin et al., 2011). In fact, bio-derived ethanol and biodiesel are already being used in several countries (typically as blends), including the United States, Brazil, Germany, Australia and several others (Lin et al., 2011).

Biodiesel, in particular, is a promising alternative fuel for diesel engines. It is believed to be a promising substitution for fossil diesels because it has similar properties to fossil diesels (Olutoye & Hameed, 2013). Moreover, compared to conventional fossil diesels, the biodegradable, renewable and non-toxic biodiesel can reduce gas emissions, especially SO_x emission because bio-feedstocks are free of or low in nitrogen and sulfur, and also CO_2-neutral (Atadashi et al., 2010; Gui et al., 2008). Due to these advantages, biodiesel has experienced a major surge worldwide in the 21 century. Figure 2.1 shows the worldwide biodiesel production from 2001 to 2011. Biodiesel production is increasing globally. Argentina, Brazil, France, Germany, and the United States of America (USA) are the top five global biodiesel producing nations (Sarma et al., 2012).

In Malaysia, annual biodiesel production has been increased from 1.1 thousand barrel per day in 2006 to 5.7 thousand barrel per day in 2009 at an average increase of 26.6% per year (Umar et al., 2013). In Brazil, the addition of 2% biodiesel (B2) in the diesel is mandatory since 2008, and is expected to increase to B5 by 2013 (Rossi et al., 2012). In the United States, biodiesel production has increased dramatically from 500 thousand gallons in 1999 to 150 million gallons in 2006 (He et al., 2006). Over 690 million gallons (Atadashi et al., 2010) and about 4 billion gallons (15 billion liters) (Ghosh et al., 2012) of biodiesel were produced in

2008 and 2009, respectively, in the USA. It is estimated that the global biodiesel market will reach 37 billion gallons by 2016, with an annual growth of 42%, and that the global annual production would be about 42 billion gallons by 2020 (Salvi & Panwar, 2012).

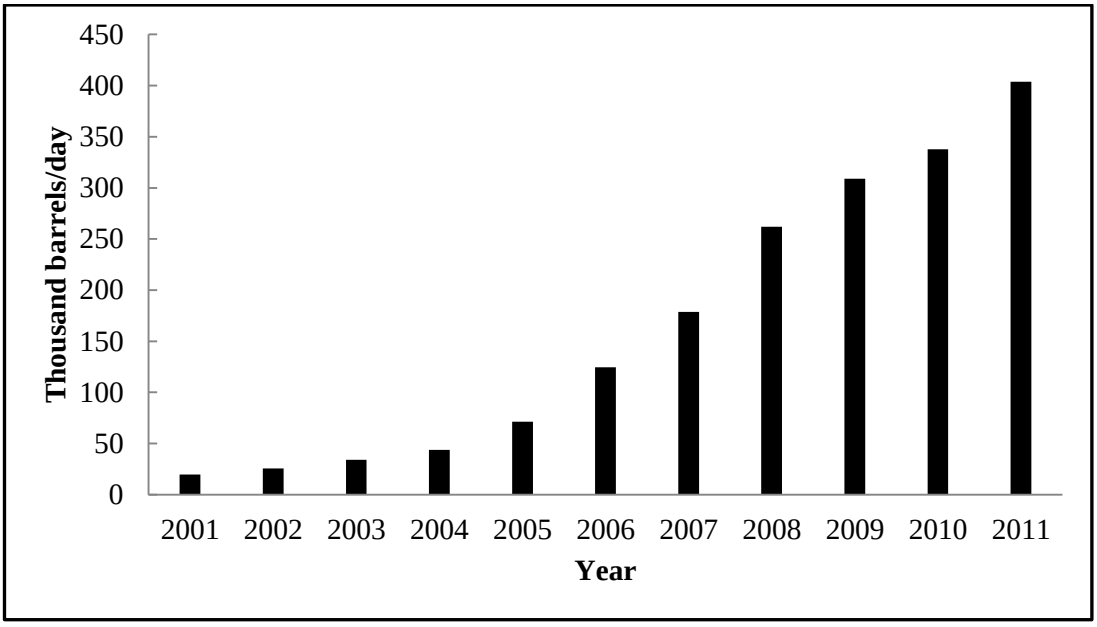
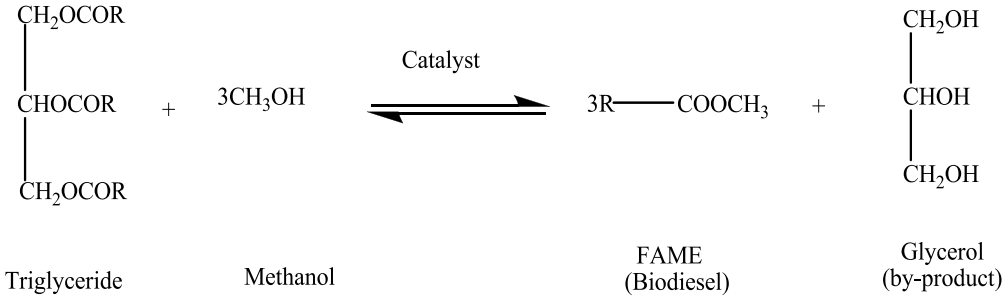


Figure 2.1 Worldwide biodiesel production from 2001 to 2011 (Salvi & Panwar, 2012)

Currently, biodiesel is commonly produced via transesterification (i.e. alcoholoysis) of vegetable oil or animal fats (triglycerides) in the presence of alkali, acid or enzyme catalyst (Yusuf et al., 2011). Briefly, transesterification is catalyzed, reversible and equilibrium reaction of triglycerides with an alcohol (usually methanol or ethanol), in which one alcohol (e.g methanol) replaces another one (e.g glycerol) from an ester. The following reaction displays the transesterification of triglycerides and methanol. Equation (2.1) and Figure. 2.2 summarize the biodiesel production process.



(2.1)

Because of the reversible nature of this reaction it can be forced to completion by using a large access of alcohol (Olutoye et al., 2011). Glycerol is produced by 10 wt% as by product from the transesterification reaction which according to the ASTM slandered for biodiesel (ASTM D-6751-02, 2002), should be almost completely removed from biodiesel. Purification of biodiesel after the transesterification reaction so that it contains less than 0.02% wt glycerol is the required to meet this standard (Lin et al., 2011).

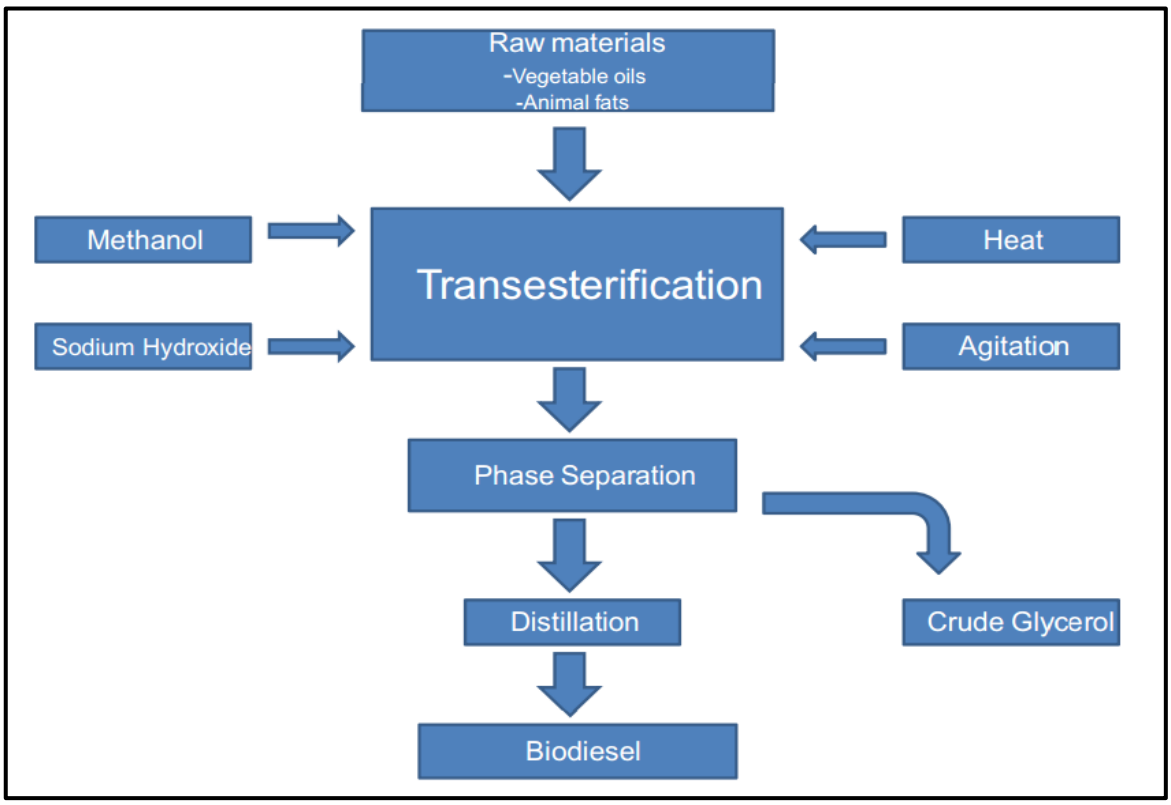


Figure 2.2 Schematic for biodiesel production process (Sarma et al., 2012)

2.1.2 Glycerol gluts

Historically, Glycerol was derived mainly from fatty acids and soap industry. Since late 1940, synthetic glycerol has been introduced to the market due to the shortage in supply which has been produced from epichlorohydrin obtained from propylene (fossil fuel origin) (Morrison, 2001). The supply map for glycerol has been changed significantly over the last ten years. After 2003, biodiesel industry became a prominent source for glycerol in the market and overcome as the biggest source for glycerol since 2008 (Taherzadeh et al., 2002). Table 2.1 shows the world production of glycerol from different sources from the period of 1992 to 2010 (Ayoub & Abdullah, 2012). As it shown in the table, fatty acid industry was a strong

source for glycerol until year 2003. After that the contribution of fatty acids industry in glycerol supply has declined and biodiesel became the main source for glycerol in 2008. The huge consumption of biodiesel in the last few years was the main reason behind the increasing trend in glycerol production. Synthetic production of glycerol decreased over the years of 1995 until 2005. After that, the production became virtually zero. The high production input cost (precursor & energy) and low price of glycerol output makes the synthetic process economically non-viable. In fact, the price of the intermediate, synthetic epichlorhydrin, is higher than glycerol. The result is the shutdown of some glycerol production plants like Dow Chemical (McCoy, 2006). Figure 2.3 shows the trend change in glycerol supply driver (Bogaart, 2009). It can be concluded from the figure that fatty acids and soap industries were the main source of glycerol before the booming of biodiesel industry during past few years. In 1999, Fatty acids, soap manufacturing process, fatty alcohol and biodiesel industry have a glycerol production ratio of 47%, 24%, 12% and 9%, respectively.

Table 2.1 World Production of glycerol from different sources (Ayoub & Abdullah, 2012)

Glycerol sources	World glycerol production ($\times 10^3$ metric tons/year)							
	1992	1995	1999	2003	2005	2006	2008	2010
Soaps	208	208	198	188	167	146	125	83
Fatty acids	271	292	313	333	396	438	479	521
Biodiesel	0	42	42	167	375	521	1125	1583
Fatty alcohol	83	104	125	104	125	167	250	250
Synthetic	83	83	63	63	21	0	0	0
Others	0	0	42	63	42	0	21	21
Total	646	729	781	917	1125	1271	2000	2458

In 2009, the picture of glycerol supply driver has been changed totally. Biodiesel industry became the biggest supply driver for glycerol where the supply percentage jumped from 9% to 64%. The fatty acids contribution dropped from 47% to 21% and the soap industry decreased its share from 24% to 6%. As the biodiesel production is increasing which is the case in the next few years, biodiesel industry will remain the main the biggest driver for glycerol (Bogaart, 2009).

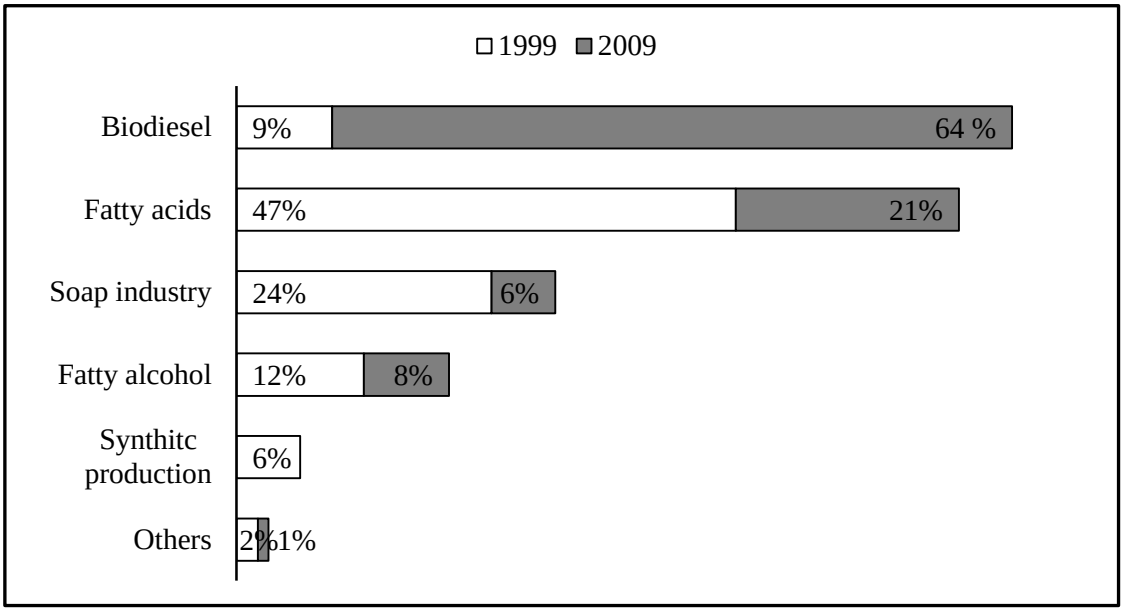


Figure 2.3 Glycerol supply driver trend change (Bogaart, 2009)

The market of glycerol is divided into two types of market, crude glycerol market and refined glycerol market. The main difference between crude and refined glycerol is the purity. The refined glycerol contains more than 95% glycerol while crude glycerol has glycerol content between 60% - 80%. Also, impurities such as ash, soap and moisture are present in higher quantities on crude glycerol.

Moreover, the acidity of crude glycerol is higher than the refined one. Table. 2.2 shows the quality parameters of the crude and refined glycerol.

In terms of demand, glycerol market is relatively small on global basis. In 2012, the global refined glycerol consumption was 1995.5 X 10^3 ton (Rossi et al., 2012). The prices of glycerol are affected by the oversupply coming from biodiesel industry. The prices of crude glycerol from biodiesel industry were fallen to zero and even negative as biodiesel producers have to pay to dispose their generated glycerol (Johnson & Taconi, 2007). However, the prices for refined glycerol didn't affected greatly by the supply of crude glycerol. Table. 2.3 show the price of different glycerol categories from 2001 to 2009 (Hazimah, 2003). It can be seen from the table that the refined and crude glycerol prices shows a downward trend from 2001 to 2007. In 2007, the price of both types shows a significant increase before it was fallen hardly in 2008 due to the global recession and excess supply of glycerol by biodiesel industry. The price of crude glycerol is expected to become lower as biodiesel production is increasing day by day.

Crude glycerol handling becomes an obstacle for the expansion of biodiesel industry. The production cost of biodiesel is around $0.50/L which is 1.5 time higher than the cost of petroleum based diesel (Johnson & Taconi, 2007). Glycerol handling contributes around 12%-14% of the total production cost of biodiesel (Johnson & Taconi, 2007). Therefore, is assumed that the biodiesel production cost is affected inversely with glycerol credit. The cost of biodiesel could be reduced by utilizing crude glycerol to produce value-added chemicals.

Table 2.2 Quality parameters of the crude and refined glycerol (Hazimah, 2003)

Parameter	Crude glycerol	Refined glycerol
Glycerol content (%)	60-80	99.1-99.8
Moisture content (%)	1.5-6.5	0.11-0.8
Ash (%)	1.5-2.5	0.054
Soap (%)	3-5	0.56
Acidity (PH)	0.7-1.3	0.1-.16
Chloride (ppm)	ND	1
Color (APHA)	Dark	34-45

Table. 2.3: Annual glycerol price from 2001 to 2009 (Ayoub & Abdullah, 2012)

Type of glycerol	Glycerol price (cent/pound)								
	2001	2002	2003	2004	2005	2006	2007	2008	2009
Synthetic	72	73	90	85	85	-	-	-	-
Refined	60	58	65	55	45	35	70.5	55	41
Crude	15	12	12	10	5	2	10	5	6

2.2 Glycerol

Glycerol is a trihydric alcohol, namely 1,2,3-propanetriol, because it has three hydrophilic hydroxyl groups. It is a colorless, odorless, sweet-tasting, syrupy or viscous liquid (Pachauri & He, 2006). It is hygroscopic, and soluble in water and ethanol. It melts at 17.8 ^{o}C and boils, with decomposition, at 290 ^{o}C. Its chemical formula is: OH-CH_2-CH (OH)-CH_2-OH. Glycerol is the principal component of triglycerides. It is a natural component of animal fats and vegetable oils (8% - 14% of their total weight), and also found in petrochemical feedstocks (Cho et al., 2010).

It is released from the triglycerides by processes such as high-pressure splitting, saponification, and transesterification (Nicol et al., 2012). High-pressure splitting is a hydrolytic technique for free fatty acids (FFAs) production; saponification is an alkali treatment of lipids to obtain soap; while transesterification is a biodiesel production process whereby fats and oils are reacted with alcohol in the presence of an alkali catalyst. Glycerol is chemically synthesized in industries. The precursor of its synthetic production is propylene which, in most cases, is chlorinated before the resulting intermediate, epichlorohydrin, is hydrogenated into glycerol (Quispe et al., 2013).

Glycerol has a wide range of industrial applications. It is used nearly in every industry. It has more than 2000 applications today including food and drinks, toothpaste, cosmetics, toiletries, plastics, tobacco, pulp and paper, paint, leather and textiles, pharmaceutical, and automotive industries. Figure. 2.4 shows the current market of glycerol by sector (Pagliaro et al., 2007).

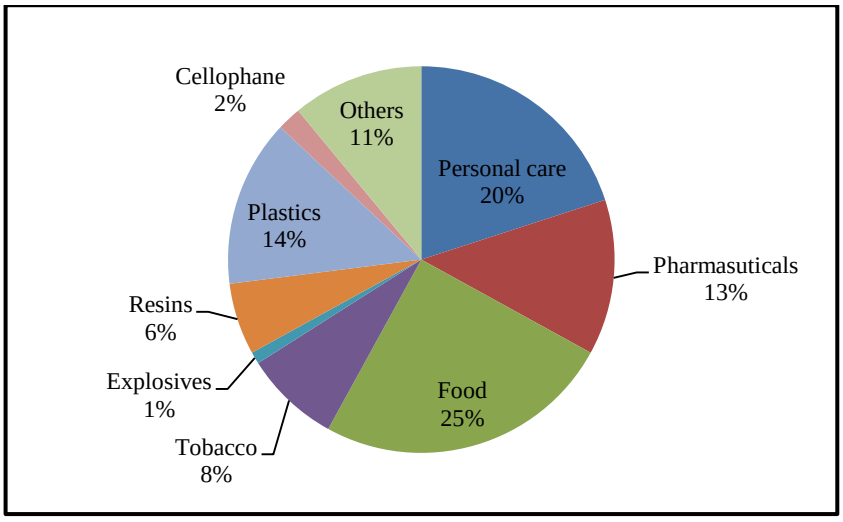


Figure. 2.4: Currant market of glycerol (Pagliaro et al., 2007)

Despite all these application of glycerol, the glycerol market cannot absorb the huge quantities of glycerol generated from biodiesel industry. Therefore, finding new uses for glycerol is necessary for the sustainability of biodiesel industry (Johnson & Taconi, 2007). Today, the conversion of glycerol to value-added chemicals is a subject of research in academia and industry.

Using glycerol as building block chemical has many advantages. First, increase the profitability of biodiesel industry by converting cheap glycerol to more valuable chemicals. Second, it will reduce the dependence on petroleum based chemicals and increasing the renewability of production of chemicals. Third, glycerol is a green chemical so that using it as feedstock is an environmental advantage for making chemicals (Zhou et al., 2008).

There is a tremendous opportunity to develop a variety of new processes and product line from glycerol taking the advantage of its unique structure and reactivity. Glycerol can be oxidized, reduced, halogenated, etherified, and esterified to obtain alternative commodity chemicals such as acroelin, such as dihydroxyacetone, mesoxalic acid, 1,3-propanediol, 1,3-dichloropropanol, glyceryl ethers, glycerol carbonate and glyceryl esters (Zheng et al., 2010). Unfortunately, many of these pathways will turn out to be unrealistic. One reason these pathways are not viable is because the current methods of production are too cheap and effective. One example of this is acrylic acid. The estimated cost to produce acrylic acid from glycerol is more than twice as expensive as the current commercial methods (Bozell et al., 2007). Similar problems occur with polyester fibers and polyurethane foams. Other potential products are not feasible because the commercial selling price is similar to the estimated raw material cost of crude glycerol. This is true for pathways that convert crude glycerol into aromatic polyester polyol foam and acetone (Johnson &

Taconi, 2007). Other pathways, such as converting glycerol into lactic acid or malonic acid, are not viable because they lack large market capacities (Johnson & Taconi, 2007). Still, all things considered, there are some promising candidates. A few of the most promising are succinic acid, 1,3-propanediol, 1,2-propanediol, polyglycerols, and glycerol carbonate (Onwudili & Williams, 2010).

2.3 Glycerol Carbonate

Glycerol carbonate is one of the promising glycerol derivatives. It is considered from cyclic carbonate family. Using glycerol as feedstock for glycerol carbonate could absorb appreciable amount from excess glycerol in the market. The annual consumption of cyclic carbonates was around 100,000 ton (Clements, 2003). Also, glycidol, most valuable glycerol carbonate derivative, market was noted at 270000 ton in United States alone in 2006 (Johnson & Taconi, 2007).

Glycerol carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane) is an organic compound categorized under cyclic carbonates family. The uniqueness of glycerol carbonate among other cyclic carbonate is the presence of two reactive sites on its molecule. These reactive sites are 2-oxo-1,3-dioxolane (ODO) group and hydroxyl group. These sites make glycerol carbonate involves in chemical reaction as electrophile or nucleophile regent (Sonnati et al., 2013). Thus, glycerol carbonate could be used as green biobased building block for a wide range of chemicals (Pagliaro et al., 2007; Tay et al., 2011). Regarding its physical properties, glycerol carbonate is stable, colourless, not flammable, water soluble, biodegradable, non toxic, and viscous liquid with low evaporation rate. The chemical properties of glycerol carbonate are shown on Appendix B.

Glycerol carbonate is considered a relatively new material to the industry and its application is still emerging (Ochoa-Gómez et al., 2012). Glycerol carbonate can be utilized as a green substitute for ethylene and propylene carbonates in a wide range of applications. Also, the wide range of reactivity of glycerol carbonate molecule attracts the attention to explore other routes to synthesize valuable chemicals using glycerol carbonate as a building block material. It can be applied directly and indirectly through its derivatives in many applications.

Glycerol carbonate can be used as solvent for different purposes. Most of the solvents available these days are fossil fuel derived solvents. Recently, much research efforts have been done to reduce the use of the volatile organic solvents and substituted with green and environmentally friendly solvents (Jessop, 2011). Glycerol carbonate has the essential physical properties to be applied as green solvent such as low volatility, low toxicity, low flammability and biodegradability. Also, the presence of hydroxyl group on glycerol carbonate molecule increase the basicity of the molecule compared to propylene carbonate and leads to water like properties. Different studies reported the use of glycerol carbonate as a solvent (Ou et al., 2012). Herault (2001) reported the use of glycerol carbonate as a general purpose biobased solvent. Lameiras et al. (2011) reported the use of glycerol carbonate as ultraviscous solvent in NMR analysis. Glycerol carbonate was tested as biosolvent for soluble enzymatic system development where it was successfully substitute the use of propylene carbonate in biocatalytic transesterification reactions (Ou et al., 2012). Also, it was used as an alternative for ionic liquids in traditional ionic liquid processes. For instance, ionic liquids has been partially substituted with glycerol carbonate in acid catalyzed dehydration of fructose and inulin to 5-hydroxymethylfurfural (Sonnati et al., 2013). The substitution of ionic liquids with

glycerol carbonate could reduce the consumptions of such hazardous materials and effects positively on the environment (Muzikar et al., 2001).

Glycerol carbonate has potential to be used as electrolyte in lithium and lithium-ions batteries. Electrolytes are used in batteries to transfer the charge (in the form of ions) between two pairs of electrodes (cathode and anode compartments). These electrolytes are formed by dissolving slats, i.e. lithium salts, in solvent, either water or organic solvent (Jeong et al., 2008; Sonnati et al., 2013).

Propylene carbonate has been selected as a good candidate as lithium ions carrier in lithium batteries (Buqa et al., 2005). A mixture of ethylene and propylene carbonates is until now the most suitable solvent for lithium batteries. The desirability of using propylene and ethylene carbonates as solvent came from its wide liquid range, high dielectric constant and static stability with lithium (Tobishima et al., 1997). The use of glycerol carbonate as solvent instead of propylene carbonate or ethylene carbonate has a lot of potential. First, glycerol carbonate has a lower cost compared to ethylene and propylene carbonate. Second, it is biobased material which has environmental advantage. Third, it is liquid over a wide range of temperature and does not freeze at room temperature like ethylene carbonate. Fourth, glycerol carbonate is by far less flammable than ethylene carbonate. Fifth, it has the highest dielectric constant compared to other carbonates solvents. Sixth, the use of glycerol carbonate could increase the longevity of the battery cell by formation of oligomers which in turn creates a passivation layers on batteries electrodes. Other than electrolytes, glycerol carbonate could be used as an additive to the electrolyte solution to increase the safety characteristics of lithium batteries (Porras et al., 2003; Ryu, 2008).

In building materials, glycerol carbonate has been incorporated in hydraulic lime and metakaolin to form green binder mixture. The addition of glycerol carbonate enhances the mechanical strength of the binder which opens the doors in manufacturing sustainable and green eco-building composites (Magniont et al., 2010). Glycerol carbonate could be used also as a curing agent for water glass manufacturing instead of ethylene or propylene carbonate (Clements, 2003).

In cosmetics, glycerol carbonate could be used as nail lacquer gel remover in combination with 1,3-dimethyl-2-imidazolidinone,hydroxypropyl cellulose and water. The formed gel is not flammable and does not crack the nails as traditional lacquer remover does, i.e. acetone and ethyl acetate. Also, glycerol carbonate may be used as a surfactant in cosmetic products such as shampoos, hair lotions, bubble baths, creams or lotions due to its biobased origin and non-toxicity (Ochoa-Gómez et al., 2012). Moreover, it can be used as plasticizer in cosmetic products such as make-up, lipsticks, nail polish and hair care. Furthermore, glycerol carbonate glycoside which could be synthesized by reacting a saccharide with glycerol carbonate under acidic conditions can be used as humectant (Pagliaro et al., 2007).

Some glycerol carbonate derivatives found its application as surfactants. For instance, glycerol esters, i.e. monoglycerides, act as valuable non-ionic surfactants for water in oil emulsions. α-monoglycerides could be synthesized by the condensation of fatty acids with glycerol carbonate in the presence of triethylamine as a catalyst (Behr et al., 2008). Polyglycerol is another glycerol carbonate derivative that can be used also as surfactant. It can be prepared from the reaction of sorbitan carboxylic acid ester with glycerol carbonate. Other than surfactant, polyglycerol can be used as emulsifiers, dispersants, thickeners, solubilizers, spreading agents,